DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/136,217 filed on May 26, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 21st day of September, 1999

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Perovskite Titanium-Type Composite Oxide Particle and Production Process Thereof

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I) and having a specific surface area of from 10 to 200 m^2/g, a primary particle thereof having a specific surface area diameter D_1 of from 10 to 100 nm as defined by formula (II) and the ratio D_2/D_1 between D_1 and the average particle size D_2 of secondary particle being from 1 to 10:

$$M(TiO_3) \qquad \text{(I)}$$

(wherein M is at least one metal selected from Ca, Sr, Ba, Pb and Mg);

$$D_1=6/\rho S \qquad \text{(II)}$$

(wherein ρ is a density of particles and S is a specific surface area of a particle).

[Claim 2] A process for producing a Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I), said process comprising reacting titanium oxide particles containing brookite crystals with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg:

$$M(TiO_3) \qquad (I)$$

(wherein M is at least one metal selected from Ca, Sr, Ba, Pb and Mg).

[Claim 3] A process for producing a Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I), said process comprising reacting a titanium oxide sol obtained by hydrolyzing a titanium salt in an acidic solution with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg:

$$M(TiO_3) \qquad (I)$$

(wherein M is at least one metal selected from Ca, Sr, Ba, Pb and Mg).

[Claim 4] The production process as claimed in claim 2 or 3, wherein the reaction for producing a Perovskite titanium-type composite oxide particle is performed in an alkali solution.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a titanium-type composite oxide particle and a production process thereof, more specifically, the present invention provides a Perovskite titanium-type composite oxide fine particle

having excellent dispersibility.

[0002]

[Background Art]

Perovskite titanium-type composite oxides represented by barium titanate are being used over a wide range as a functional material such as dielectric material, stacked ceramic capacitor and piezoelectric material. With the advancement of downsizing and reduction in weight of electronic parts, it is demanded to develop a process for obtaining a titanium-type composite oxide particle having a smaller particle size and excellent dispersibility at a low cost.

[0003]

For producing titanium-type composite oxide, a solid phase process of using an oxide or carbonate as a starting material, mixing the powder thereof in a ball mill or the like and reacting it at a high temperature of about 800°C or more to produce a composite oxide, an oxalate process of preparing an oxalic acid composite salt and thermally decomposing the salt to obtain a titanium-type composite oxide, an alkoxide process of using metal alkoxide as a starting material and hydrolyzing it to obtain a precursor, or a hydrothermal synthesis of reacting a starting material in a water solvent at a high temperature and high pressure to obtain a precursor is used. Also, a process of preparing

titanium oxide or a precursor thereof, dispersing it in a solvent and compounding it with an objective element in a solution (see, JP-A-8-119633 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and a process of using titanium tetrachloride, titanium sulfate or the like as the titanium starting material (see, JP-A-59-39726) are known.

[0004]

[Problems to be Solved by the Invention]

The solid phase process is industrially advantageous because of low production cost, however, the titanium-type composite oxide produced is large in the particle size and not uniform, accordingly, not suitable for functional materials such as dielectric material and piezoelectric material. In the oxalate process, the particle size is smaller than that obtained by the solid phase process, however, the particle is still on the order of from 0.2 to 0.5 μm. According to the alkoxide process, the particles having a particle size of approximately from 20 to 30 nm may be obtained, however, due to use of an organic material as the starting material, the production cost is high. The hydrothermal synthesis is disadvantageous in that the reaction is performed at a high temperature and a high pressure, therefore, a dedicated facility is necessary and the cost increases.

Furthermore, even if particles having a small particle size are obtained by these processes, unless the particles have good dispersibility at the same time, they coagulate in a solvent and when formed and sintered into a product, properties necessary for the functional material such as dielectric material and piezoelectric material cannot be satisfactorily brought out.

[0005]

The present invention has been made under these circumstances and the object of the present invention is to provide a Perovskite titanium-type composite oxide particle having a small particle size and excellent dispersibility at a low cost.

[0006]

[Means to Solve the Problems]

The above-described object can be attained by the invention of claim 1, which is a Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I) and having a specific surface area of from 10 to 200 m^2/g, a primary particle thereof having a specific surface area diameter D_1 of from 10 to 100 nm as defined by formula (II) and the ratio D_2/D_1 between D_1 and the average particle size D_2 of secondary particle being from 1 to 10:

$M(TiO_3)$ (I)

(wherein M is at least one metal selected from Ca, Sr, Ba, Pb and Mg);

$$D_1=6/\rho S \quad (II)$$

(wherein ρ is a density of particles and S is a specific surface area of a particle);

the invention of claim 2, which is a process for producing a Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I), the process comprising reacting titanium oxide particles containing brookite crystals with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg; and

the invention of claim 3, which is a process for producing a Perovskite titanium-type composite oxide particle comprising a composition represented by formula (I), the process comprising reacting a titanium oxide sol obtained by hydrolyzing a titanium salt in an acidic solution with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg.

The production process described above is preferably performed in an alkali solution.

[0007]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The titanium-type composite oxide particle of the

present invention comprises a composition represented by formula (I). The ratio D_2/D_1 of the specific surface area diameter D_1 of a primary particle thereof to the average particle size D_2 of the secondary particles is from 1 to 10. At the same time, the titanium-type composite oxide particle has a Perovskite crystal structure. The specific surface area diameter D_1 of a primary particle can be obtained according to formula (II). In formula (II), ρ is a density of particles and S is a specific surface area of a particle measured by the BET method. The average particle diameter D_2 of secondary particles is a value determined using a particle size distribution meter by dispersing the titanium-type composite oxide in a solvent. The particle size distribution is usually measured by a centrifugal precipitation method, an electrozone method (Coulter counter), a light scattering method or the like. Among these, the light scattering method is preferred. The smaller the value of D_2/D_1 calculated is, the more excellent the dispersibility of particles is. The value of D_2/D_1 cannot be theoretically less than 1 when the particle is spherical. On the other hand, if the value exceeds 10, the primary particles become poor in the dispersibility and disadvantageously undertake coagulation.

The titanium-type composite oxide of the present invention has D_2/D_1 of from 1 to 10 and ensures good

dispersibility of primary particles.

$$M(TiO_3) \qquad (I)$$

(wherein M is at least one metal selected from Ca, Sr, Ba, Pb and Mg);

$$D_1=6/\rho S \qquad (II)$$

[0008]

The production process of the present invention is described below.

The titanium oxide particles containing brookite crystals for use in the present invention may be brookite titanium oxide alone or may contain rutile or anatase titanium oxide as long as it contains brookite crystals. In the case where the titanium oxide particles contain rutile or anatase titanium oxide, the ratio of the brookite titanium oxide in the titanium oxide is not particularly limited, however, it is usually from 1 to 100 wt%, preferably from 10 to 100 wt%, more preferably from 50 to 100 wt%. The ratio in these ranges is preferred because crystalline particle is more facilitated in the simple grain formation than amorphous particle and advantageous for obtaining titanium particles having excellent dispersibility in a solvent, and particularly brookite titanium oxide has excellent dispersibility. The reason thereof is not known, however, it is considered that the

higher zeta potential of brookite than that of rutile or anatase has some relation thereto.

[0009]

Examples of the production process of titanium oxide particles containing brookite crystals include a production process in the gaseous phase, where anatase titanium oxide particles are heat treated to obtain titanium oxide particles containing brookite crystals, and a production process in the liquid phase, where a solution of a titanium compound such as titanium tetrachloride, titanium trichloride, titanium alkoxide and titanium sulfate is neutralized or hydrolyzed to obtain a titanium oxide sol having dispersed therein titanium oxide particles.

The production process is not particularly limited as long as the titanium oxide particles obtained contain brookite crystals. When using the thus-obtained titanium oxide particles containing brookite crystals, a titanium-type composite oxide is produced, the particle has a small particle size and excellent dispersibility. Therefore, a process of hydrolyzing a titanium salt in an acidic solution to obtain a titanium oxide sol, which is previously found by the present inventors, is preferably used. More specifically, a process of adding titanium tetrachloride to hot water at from 75 to 100°C and hydrolyzing the titanium tetrachloride at a temperature of

from 75°C to the boiling point of the solution while controlling the chloride ion concentration to obtain titanium oxide particles containing brookite crystals in the form of a titanium oxide sol (Japanese Patent Application No. 9-231172) or a method of adding titanium tetrachloride to hot water at from 75 to 100°C and hydrolyzing the titanium tetrachloride in the presence of one or both of nitrate ion and phosphate ion at a temperature of from 75°C to the boiling point of the solution while controlling the total concentration of chloride ion, nitrate ion and phosphate ion to obtain titanium oxide particles containing brookite crystals as a titanium oxide sol (Japanese Patent Application No. 10-132195) is preferred.

[0010]

The thus-obtained titanium oxide particles containing brookite crystals usually have a size of from 5 to 50 nm in terms of the specific surface area diameter of a primary particle. If the specific surface area diameter of a primary particle exceeds 50 nm, the titanium-type composite oxide particles produced using such titanium oxide particles are increased in the particle size and not suited for functional materials such as dielectric material and piezoelectric material. On the other hand, if it is less than 5 nm, there arise difficulties in the handling during

the process for producing titanium oxide particles.

[0011]

In the production process of the present invention, when a titanium oxide sol obtained by hydrolyzing a titanium salt in an acidic solution is used, the titanium oxide particle in the sol obtained is not particularly limited to the crystal form and the crystal form is not limited to brookite.

In the case where a titanium salt such as titanium tetrachloride or titanium sulfate is hydrolyzed in an acidic solution, the reaction is restrained and proceeds at a lower rate than the reaction in a neutral or alkaline solution. As a result, the particle size becomes simple and the titanium oxide sol obtained exhibits excellent dispersibility. Furthermore, anion such as chloride ion and sulfate ion is scarcely taken in inside the titanium oxide particle produced, accordingly, when a titanium-type composite oxide is produced, mixing of anion into the particle can be reduced.

On the other hand, if the hydrolysis is performed in a neutral or alkaline solution, the reaction rate elevates and a large number of nuclei are generated at the initial stage. As a result, despite the small particle size, the titanium oxide sol obtained is poor in the dispersibility and the particles coagulate like cloud. If a titanium-type

composite oxide is produced starting from such a titanium oxide sol, the particles obtained are poor in the dispersibility despite the small particle size. Furthermore, anion is readily mixed inside the titanium oxide particle and the anion is difficult to remove in the later steps.

[0012]

The method for hydrolyzing a titanium salt in an acidic solution to obtain a titanium oxide sol is not particularly limited as long as the solution can be maintained acidic. However, a method of using a titanium tetrachloride as a starting material, hydrolyzing it in a reactor equipped with a reflux condenser, inhibiting the escape of chlorine generated there and thereby maintaining the solution acidic, which is found by the present invention, is preferred (Japanese Patent Application No. 8-230776).

The concentration of titanium salt as the starting material in the acidic solution is preferably from 0.01 to 5 mol/ℓ. If the concentration exceeds 5 mol/ℓ, the hydrolysis reaction rate increases, as a result, the particle size is large and the titanium oxide sol obtained is poor in the dispersibility, whereas if it is less than 0.01 mol/ℓ, the titanium oxide concentration becomes low and the productivity decreases.

[0013]

The metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg, for use in the production process of the present invention is not particularly limited as long as it contains the above-described metal. The metal salt is preferably water-soluble and usually, a nitrate, an acetate, a chloride or the like is used. One kind of metal salt may be used or two or more kinds of metal salts may be mixed at an arbitrary ratio. More specifically, in the case of Ba, barium chloride, barium nitrate, barium acetate or the like may be used, and in the case of Sr, strontium chloride, strontium nitrate, strontium acetate or the like may be used.

[0014]

The process for producing a titanium-type composite oxide particle of the present invention comprises reacting a titanium oxide sol obtained by hydrolyzing titanium oxide particles containing brookite crystals or hydrolyzing a titanium salt, in an acidic solution with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg. The reaction conditions are not particularly limited but in usual, the reaction is preformed in an alkali solution. The pH of the solution is preferably 13.0 or more, more preferably from 14.0 or more. By setting the pH to 14.0 or more, a titanium-type composite oxide

particle having a smaller particle size can be produced.

The reaction solution is rendered alkaline by adding an alkali compound. The alkali compound added is not particularly limited. However, if an alkali metal hydroxide such as lithium hydroxide, sodium hydroxide and potassium hydroxide is added, an alkali metal remains in the titanium-type composite oxide obtained and when this composite oxide is formed and sintered into a product, the capability and piezoelectric material may be deteriorated for functional materials such as dielectric material and piezoelectric material. Because of this reason, an organic alkali compound such as ammonium tetramethylhydroxide is preferably added.

[0015]

The solution is preferably prepared such that the concentration of titanium oxide particle or titanium oxide sol is from 0.1 to 5 mol/ℓ and the concentration of metal salt containing M is from 0.1 to 5 mol/ℓ in terms of the metal oxide.

[0016]

While stirring the thus-prepared alkali solution, the reaction is performed at an atmospheric pressure under heating for maintaining the temperature usually at from 40 to 120°C, preferably from 80 to 120°C. The reaction time is usually 1 hour ore more, preferably 4 hours or more. After

the completion of reaction, the slurry is washed with water if required for the removal of impurity ion or the like. Thereafter, the slurry is filtered and dried and then may be calcined. The drying is usually performed at a temperature of from room temperature to 150°C for from 1 to 24 hours. The drying atmosphere is not particularly limited and the drying is usually performed under atmospheric pressure or reduced pressure. The calcination is performed to improve the crystallinity of the titanium-type composite oxide and at the same time to remove the remaining impurities including anion such as chloride ion, sulfate ion and phosphate ion, and alkali compounds such as ammonium tetramethyl hydroxide. The calcination is usually performed at a temperature of from 300 to 1,000°C. The calcining atmosphere is not particularly limited and the calcination is usually performed in air.

The thus-produced titanium-type composite oxide particle is a small particle having Perovskite crystal system, where the specific surface area of from 10 to 200 m^2/g, the specific surface area diameter of a primary particle is from 10 to 100 nm, and the ratio D_2/D_1 of the specific surface area diameter D_1 of a primary particle to the average particle size D_2 of secondary particles is from 1 to 10. The particles have excellent dispersibility.

[0017]

[Examples]

The present invention is described in greater detail below by referring to Examples.

Example 1:

To a reactor with a reflux condenser, an aqueous solution having a titanium tetrachloride (purity: 99.9%) concentration of 0.25 mol/ℓ was charged and heated to a temperature in the vicinity of the boiling point while preventing chloride ion from escaping and maintaining the solution acidic. At the same temperature, the titanium tetrachloride was hydrolyzed for 60 minutes to obtain a titanium oxide sol. Fig. 1 shows a photograph by a transmission type electron microscope of the titanium oxide sol obtained. From Fig. 1, the particles in the sol are monodisperse particles having a particle size of about 15 nm. This sol was condensed by sedimentation. To 320 g of the resulting sol having a titanium oxide concentration of 10 wt%, 97.7 g of barium chloride dihydrate (produced by Kokusan Kagaku K.K.) and further 600 g of ammonium tetramethyl hydroxide (aqueous solution) in a concentration of 20 wt% was added to adjust the pH to 14, and the solution was stirred for 1 hour. Thereafter, the slurry was heated to 110°C and then reacted while keeping the temperature. The precipitate in the slurry was washed with

water, filtered and dried at 150°C for 12 hours to obtain fine particle powder.

This powder was subjected to the examination of X-ray diffraction using an X-ray diffraction apparatus manufactured by Rigaku Denki K.K. (RAD-B, rotor flex), as a result, the powder obtained was found to be cubic Perovskite $BaTiO_3$. The specific surface area determined by the BET method was 34 m^2/g and the specific surface area diameter D_1 calculated by formula (II) was 0.03 μm. Furthermore, the powder was dispersed in water and the average particle size D_2 was measured by a particle counter by light scattering method manufactured by Otsuka Denshi (ELS-8000) and found to be 0.21 μm. Therefore, the ratio D_2/D_1 was 7.0.

[0018]

Example 2:

A titanium oxide sol comprising monodisperse particles having a particle size of about 8 nm was prepared in the same manner as in Example 1. Using this sol, cubic Perovskite $BaTiO_3$ fine particle powder was obtained in the same manner as in Example 1. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 46 m^2/g, the specific surface area diameter D_1 was 0.02 μm, and the average particle size D_2 was 0.19 μm. Therefore, the ratio D_2/D_1 was 9.5.

[0019]

Example 3:

A titanium oxide sol comprising monodisperse particles having a particle size of about 10 nm was prepared in the same manner as in Example 1 except that titanium sulfate was used in place of titanium tetrachloride and sulfate ion was prevented from escaping in place of chloride ion. Using this sol, cubic Perovskite $BaTiO_3$ fine particle powder was obtained in the same manner as in Example 1. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 40 m^2/g, the specific surface area diameter D_1 was 0.03 μm, and the average particle size D_2 was 0.22 μm. Therefore, the ratio D_2/D_1 was 7.3.

[0020]

Example 4:

A titanium oxide sol comprising monodisperse particles having a particle size of about 15 nm was prepared in the same manner as in Example 1. Using this sol, cubic Perovskite $SrTiO_3$ fine particle powder was obtained in the same manner as in Example 1 except that 106.7 g of strontium chloride hexahydrate was used in place of barium chloride. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 28 m^2/g, the specific surface area diameter

D_1 was 0.05 μm, and the average particle size D_2 was 0.10 μm. Therefore, the ratio D_2/D_1 was 2.

[0021]

Comparative Example 1:

A titanium oxide sol was obtained in the same manner as in Example 1 except that a solution obtained by ammonium hydroxide to an aqueous solution having a titanium tetrachloride (purity: 99.9%) concentration of 2.5 mol/ℓ and adjusted to a pH of 7 was charged to a reactor with a reflux condenser. Fig. 2 shows a photograph by a transmission type electron microscope of the titanium oxide sol obtained. From Fig. 1, the primary particles in the sol were found to be coagulated particles having a particle size of about 5 nm. Using this sol, cubic Perovskite $BaTiO_3$ fine particle powder was obtained in the same manner as in Example 1. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 58 m^2/g, the specific surface area diameter D_1 was 0.02 μm, and the average particle size D_2 was 0.25 μm. Therefore, the ratio D_2/D_1 was 12.5.

[0022]

Comparative Example 2:

Cubic Perovskite $BaTiO_3$ fine particle powder was obtained in the same manner as in Example 1 except for using 320 g of a 10 wt% aqueous solution in which a

commercially available titanium sol (F-4 produced by Showa Titanium K.K., specific surface area size: 28 nm) was thoroughly dispersed by an ultrasonic wave as titanium oxide. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 28 m^2/g, the specific surface area diameter D_1 was 0.04 μm, and the average particle size D_2 was 0.44 μm. Therefore, the ratio D_2/D_1 was 11.0.

[0023]

Comparative Example 3:

To an aqueous solution having a titanium tetrachloride (purity: 99.9%) concentration of 2.5 mol/ℓ, barium nitrate was added to give an equimolar amount to titanium within the aqueous solution and further potassium hydroxide was added thereto to adjust the pH to 13.5. The resulting solution was heated while stirring to a temperature in the vicinity of the boiling point and reacted for 4 hours while keeping the temperature. The slurry obtained was washed with water, filtered and dried at 150°C for 12 hours to obtain cubic Perovskite $BaTiO_3$ fine particle powder. This powder was examined in the same manner as in Example 1, as a result, the specific surface area determined was 28 m^2/g, the specific surface area diameter D_1 was 0.04 μm, and the average particle size D_2 was 0.45 μm. Therefore, the ratio D_2/D_1 was 11.3.

[0024]

The Perovskite titanium-type composite oxide particles obtained above by the production process of the present invention had a small particle size and excellent dispersibility. These particles could be produced starting from inexpensive titanium tetrachloride or titanium sulfate.

[0025]

[Effects of the Invention]

The titanium-type composite oxide particle of the present invention is a Perovskite titanium-type composite oxide particle having a specific surface area of from 10 to 200 m^2/g, a primary particle thereof having a specific surface area diameter D_1 of from 10 to 100 nm and the ratio D_2/D_1 between D_1 and the average particle size D_2 of secondary particle being from 1 to 10, which is favored with a small particle size and excellent dispersibility.

In the production process of the present invention, titanium oxide particles containing brookite crystals or a titanium oxide sol obtained by hydrolyzing a titanium salt in an acidic solution is reacted with a metal salt containing at least one metal selected from Ca, Sr, Ba, Pb and Mg, accordingly, a Perovskite titanium-type composite oxide particle having a small particle size and excellent dispersibility can be produced at a low cost. Furthermore, in this production process, the reaction solution is

rendered alkaline, therefore, particles having a smaller particle size can be obtained.

[BRIEF DESCRIPTION OF DRAWINGS]

[FIG. 1]

Fig. 1 is a photograph by a transmission type electron microscope of titanium oxide particles in the titanium oxide sol obtained in Example 1.

[FIG. 2]

Fig. 2 is a photograph by a transmission type electron microscope of titanium oxide particles in the titanium oxide sol obtained in Comparative Example 1.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a Perovskite titanium-type composite oxide particle having a small particle size and excellent dispersibility at a low cost.

[MEANS TO SOLVE THE PROBLEM]

A Perovskite titanium-type composite oxide particle represented by the formula: $M(TiO_3)$, having a specific surface area of from 10 to 200 m^2/g, a primary particle thereof having a specific surface area diameter D_1 of from 10 to 100 nm and the ratio D_2/D_1 between D_1 and the average particle size D_2 of secondary particle being from 1 to 10 (in the formula, M is at least one selected from Ca, Sr, Ba, Pb and Mg). Also, a production process of reacting titanium oxide particles containing brookite crystals or a titanium oxide sol obtained by hydrolyzing a titanium salt in an acidic solution, with a metal salt containing M above to produce a Perovskite titanium-type composite oxide particle. In this production process, the reaction may be performed in an alkali solution.

[SELECTED DRAWING] None.